DANGEROUS AND HARMFUL MATERIALS IN AGRICULTURAL SOIL AND CULTIVATED CROPS IN THE MUNICIPALITY OF PROKUPLJE

Radmila Pivić[1], Jelena Maksimović[1] Aleksandra Stanojković-Sebić[1], Zoran Dinić[1]

[1]*Institute of Soil Science, Belgrade, Teodora Drajzera 7, Republic of Serbia*
e-mail: drradmila@pivic.com

Abstract
In the area of the Municipality of Prokuplje in the Republic of Serbia, in the period July-November 2019, 26 samples of soil and aboveground part of plant material found at the research sites were sampled. In the laboratory of the Institute of Soil Science, Belgrade, a test of the content of hazardous and harmful substances in the sampled soil and plant material was conducted. The analyzed plant cultures are used partly for human consumption (fruits), one part is used for human and animal nutrition (cereals, corn), and one part belongs to animal feed (grass mixture). The study was aimed to examine the possibility that hazardous and harmful substances enter the food chain. The obtained values of the tested trace elements in the plant material are low at most of the examined localities, even on plots with increased content of total forms of tested elements in the soil, there are no increased contents in plant material, except at one locality where Pb content was found in wheat. In this specific sample, value was above (MPC) the maximum permitted concentrations ($Pb=0.94\ mg \cdot kg^{-1}$), which is recommended to be excluded for human consumption.

Key words: soil, plant material, hazardous and harmful substances

Introduction
Heavy metals are present in traces in all unpolluted soils as a result of decomposition of the parent substrate and are therefore widespread in soils, plants and animals. Studies have shown that especially in urban and industrial areas there has been a significant increase in the content of heavy metals in the soil [1]. A special problem is represented by metals that accumulate in the human body through food, through the food chain, such as cadmium and lead. Land is a dynamic system in balance with the environment and needs to be protected from further degradation. Plants are a mediator through which elements from the soil, and partly from water and air, are transmitted to the human body. Some of the elements are necessary for the growth and development of plant cultures and without them they cannot survive, some have a stimulating effect, while one group of elements at higher concentrations has a very toxic effect on plants.

Material and Methods
The total number of locations where the composite soil sample was sampled in the period July-November 2019 was 26. Number of samples of found plant material (aboveground part of the vegetative mass) was 32. From total number of samples, three samples of corn plant mass were sampled in milky and waxy maturity. The plant material at location 24 consisted of four fruit species, so that the chemical properties were tested for each plant species found at the sampling site. Figure 1 shows the layout of the sampling sites. In the laboratory, composite soil samples were dried and passed through a Ø 2 mm sieve [2]. Determination of trace elements in ICP-AES soil extracts - Total concentrations of the most significant hazardous (As, Cd, Cr, Ni, Pb, Co) and harmful elements (Cu, Zn, Fe), by the method of ISO 22036: 2008; Available forms of Fe, Mn, Zn, Cu - DTPA buffer solution extraction and determination by ICP using method: SRPS ISO 14870: 2005. Analyzed aerial parts of the study plant species were dried for 2 hours

at 105^{o}C, using gravimetric method for determination of dry matter content of plant tissue. The dry matter determination is used to correct the sample element concentration to an absolute dry matter basis [3]. The content of heavy metals (Pb, Ni, Cr and Cd) in selected plants was determined with an inductively coupled plasma optical emission spectrometer ICAP 630 (ICP-OES), after the samples were digested with concentrated HNO_3/H_2O_2 for total form extraction.

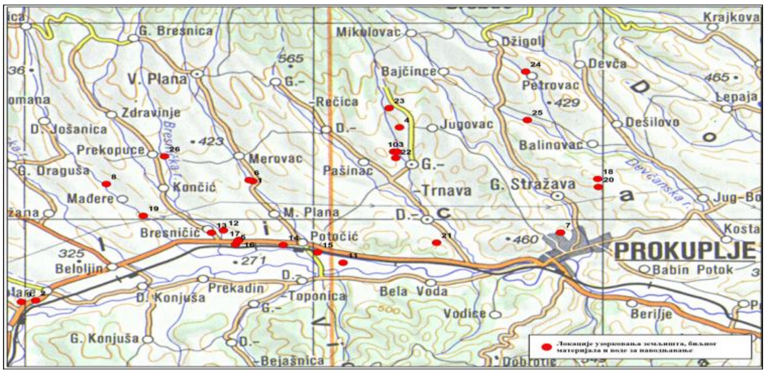

Figure 1. Sampling sites (source: Institut of Soil Science, 2019.)

Results and discussion

For interpretation of the maximum allowable concentrations (MPC) of the total forms of the tested elements, for soil samples, the values shown in Table 1 were used.

Table 1. Maximum permitted concentrations (MPC) of total forms of hazardous and harmful substances in the soil in the Republic of Serbia

Element/Rule book	Cd	Co	Cr	Mn	Ni	Pb	Zn	Cu	As
			($mg\ kg^{-1}$) absolutely dry matter						
Official Gazette 23/1994 [4]	3		100		50	100	300	100	25
Kastori et al.(1997) [5]				400*					
Ordinance - Official Gazette 51/2002 [6]		30*							

Tables 2 and 3 show the mean value, the range of the analyzed total forms of the examined elements and the number of locations where the content above the MPC was determined in the soil samples at both sampling depths (0-30 cm and 30-60 cm).

Table 2. The content of total forms trace elements in soil samples (0-30 cm)

Element	Cd	Co	Cr	Mn	Ni	Pb	Zn	Cu	As
					($mg\ kg^{-1}$)				
Range	0,21 - 0,42	9,93 - 18,2	19,2 - 84,3	354-890	15,9-97,6	9,28-74,6	37,2-78,8	12,2-89,2	2,06-24,4
Average	0,30	14,9	56,8	579	54,1	18,3	56,7	25,4	8,04
N^{o} of location Above MPC	0	0	0	25	17	0	0	0	1

Table 3. The content of total forms trace elements in soil samples (30-60 cm)

Element	Cd	Co	Cr	Mn	Ni	Pb	Zn	Cu	As
					($mg\ kg^{-1}$)				
Rang	0,20 - 0,43	10,3 - 18,5	19,6-91,6	391 - 955	16,8 - 101	7,06 - 66	38,4-99,4	11,3-69,9	1,68-20,7
Average	0,30	15,2	58,6	581	55,6	17,8	58,7	25,3	7,66
N^{o} of location Above MPC	0		0	25	16	0	0	0	1

In all examined soil samples, the content of total forms of Mn above the maximum permissible concentrations (MPC) was determined at both sampling depths (0-30 cm and 30-60 cm), except at location 21, where it was in the permitted concentrations. Ni content was above MPC at

location number 1 in the first sampling depth, location no. 2 in the second sampling depth, and at both sampling depths at locations no. 4, 8, 9, 14, 15, 17, 18, 19, 20, 21, 22, 24. The content of As was above the MPC at both sampling depths only at location N° 24. The content of other examined elements is within the limits of the MPC. The appearance of the content of individual elements above the MPC can be partly caused by geophysical origin and partly by anthropogenic factors, therefore, research the causes of the occurrence of these concentrations aove the permitted values should be investigated in more details.
Table 4 shows the levels of content provision of accessible forms of the tested elements in the soil samples and in Tables 5 and 6 the contents at the test depths.

Table 4. Limit values of accessible microelements in soil

Limit values	Cu	Zn	Fe	Mn
		(mg kg^{-1})		
very low	<0,3	<0,5	0-5	0-4
low	0,3-0,8	0,5-1	5-10	4-8
medium	0,9-1,2	1-3	11-16	9-12
high	1,3-2,5	3-6	17-25	13-30
very high	>2,5	>6	>25	>30

Table 5. The content of available forms trace elements in soil samples (0-30 cm)

Grade	Cu	N° samples	Fe	N° samples	Mn	N° samples	Zn	N° samples
very low	<0,3	0	0-5		0-4	0	< 0,5	2
low	0,3-0,8	0	5-10	0	4-8	0	0,5-1	12
medium	0,9-1,2	0	11-16	3	9-12	3	1-3	11
high	1,3-2,5	14	17-25	2	13-30	9	3-6	1
very high	>2,5	12	>25	21	>30	14	>6,0	0
Rang		1,54 – 18,5		11,0 – 87,5		7,60 – 54,2		0,35 – 3,67
Average		3,52		45,2		30,1		1,10

Table 6. The content of available forms trace elements in soil samples (30-60 cm)

Grade	Cu	N° samples	Fe	N° samples	Mn	N° samples	Zn	N° samples
very low	<0,3	0	0-5	0	0-4	0	< 0,5	5
low	0,3-0,8	0	5-10	0	4-8	0	0,5-1	8
medium	0,9-1,2	0	11-16	1	9-12	3	1-3	12
high	1,3-2,5	12	17-25	2	13-30	6	3-6	1
very high	>2,5	14	>25	23	>30	17	>6,0	0
Rang		1,07 – 24,1		11,5 - 144		11,0 – 69,6		0,13 – 4,80
Average		3,93		54,5		35,1		1,13

The content of accessible forms of Cu in the tested soil samples at a depth of 0-30 cm in 88% of the tested samples is very high while in 12% it is high; the content of available Fe is very high in 96% of the samples and high in 4%; the content of accessible Mn in 72% of samples is very high, 24% high, 4% medium; the content of available Zn is high in 12% of samples, 68% medium, 12% low and 8% very low. At a depth of 30-60 cm, the content of accessible forms of Cu is very high in 76% of the examined samples, 24% high; affordable Fe 96% very high, 4% high; accessible Mn 64% very high, 32% tall, 4% medium; affordable Zn 4% very high, 40% medium, 48% low and 8% very low.

The obtained values of the tested trace elements in the plant material are low at most of the examined localities, even on plots with increased content of total forms of tested elements in the soil there are no increased contents in the plant.
The exception is the content of the examined trace elements registered at locality number 13, where wheat was sampled. The Pb content above the MPC (Pb = 0.94 mg kg-1) was determined in the tested plant material.The results of chemical analyzes of plant mass were compared with the limit values taken from the literature [8-10]. The classifications are shown in Table 7.
Based on the limit values for human and animal nutrition, wheat should not be used in human nutrition but can be used for animal nutrition. Other tested elements in the examined plant material were within the maximum permitted concentrations.

Table 7. Optimal values of tested elements in samples of plant material for human and animal nutrition

Type of use	Plant species	MPC in plant material				
		Pb	Ni	Cr (mg kg^{-1})	Cd	Fe
Values for human consumption	plum	0,1	0,1-5*	0,1-1*	0,05	30
	cherry	0,1	0,1-5*	0,1-1*	0,05	30
	strawberry	0,1	0,1-5*	0,1-1*	0,05	30
	blackberry	0,1	0,1-5*	0,1-1*	0,05	30
	raspberry	0,1	0,1-5*	0,1-1*	0,05	30
	cereals	0,2	0,1-5*	0,1-1*	0,2	/
	corn	0,2	0,1-5*	0,1-1*	0,1	/
Values for animal feed	grass mixture	40	50	/	1	/
	cereals	40	50	/	1	/
	corn	40	50	/	1	/

* Optimal values of trace element content

Table 8 shows the individual values of the examined content of trace elements in the plant material in the study area.

Table 8. Content of trace elements in plant material

Location	Plant species	Content of trace elements in plant material				
		Pb	Ni	Cr (mg kg^{-1})	Cd	Fe
1	2	3	4	5	6	7
1	Plum	0,02	0,07	0,014	0,028	0,96
2	Plum	0,03	0,09	0,007	0,017	1,06
3	Plum	0,05	0,09	BLMD	0,009	0,74
4	Plum	0,01	0,07	0,012	0,003	1,08
5	Plum	0,03	0,16	BLMD	0,012	1,25
6	Cherry	0,00	0,02	0,007	0,003	1,63
7	Cherry	0,02	0,05	BLMD	0,002	2,38
8	Cherry	0,02	0,03	BLMD	0,019	2,68
9	Cherry	0,03	0,11	BLMD	0,015	2,54
10	Cherry	0,02	0,03	0,003	0,008	2,25
11	Grass mixture	0,28	2,15	0,772	0,064	136
12	Strawberry	0,09	0,10	0,041	0,014	14,0
13	Weath/ Cereals	0,94	0,86	0,122	0,088	39,7
1	2	3	4	5	6	7
14	Grass mixture	0,71	1,97	1,755	0,045	216
15	Blackberry	0,02	0,12	0,183	0,005	3,52
16	Raspberry	0,01	0,34	0,080	0,010	3,34

17	Raspberry	0,03	0,60	0,006	0,015	4,71
18	Cereals	0,18	0,36	0,468	0,034	31,5
19	Grass mixture	0,38	2,29	2,855	0,015	546
20	Grass mixture	0,60	3,44	4,525	0,035	1442
21	Grass mixture	0,31	3,66	1,267	0,198	224
22	Corn-tree	0,24	0,66	1,045	0,085	70,1
	Corn-grain	BLMD	0,32	0,081	0,111	14,7
23	Corn-tree	0,08	0,80	1,435	0,120	98,9
	Corn-grain	BLMD	0,55	0,225	0,081	16,2
24	Plum	BLMD	0,193	BLMD	BLMD	3,66
	Apple	BLMD	0,019	BLMD	BLMD	1,41
	Plum	BLMD	0,091	BLMD	BLMD	1,14
	Pear	BLMD	0,148	0,054	BLMD	1,89
25	Corn-tree	0,26	0,97	1,79	0,065	129
	Corn-grain	BLMD	0,60	0,213	0,085	13,5
26	Cereals	0,086	0,49	0,262	0,074	28,6

BLMD-below the limit of the method detection

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